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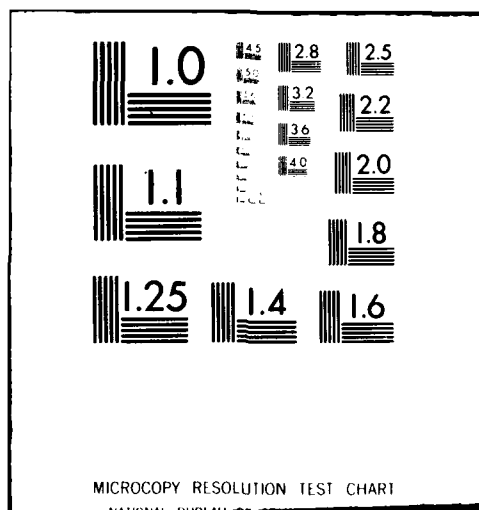
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DISPOSAL OF SOLUBLE SALT WASTE FROM COAL GASIFICATION, (U)
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DISPOSAL OF SOLUBLE SALT WASTE FROM
COAL GASIFICATION

JUN 1980

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INTRODUCTION

Energy predictions from various sources indicate a short-fall. Attention has, therefore, become focused on the use of coal as a partial solution, with subsequent realization that numerous aspects of coal utilization need to be studied. Among these aspects is the production of gas from coal. In such a study, restrictions on degrading the environment have a direct bearing on discharge of water from the plants, this largely by virtue of the solids content of the water. Increasing tightness of environmental restrictions leads to a probable requirement for zero discharge of liquid effluents. A suggested method of achieving this is examined in this paper.

For the waste disposal of salty water, ocean dumping may seem an obvious solution. However, ocean dumping is gradually being outlawed and is not at all available to most of the geographical areas of the world. For land areas (this applies to the bulk of the world's industry) the ocean dumping counterpart is stream or river dumping. This is restricted by regulation and becomes a matter of negotiation and controversy for all but the cleanest of salty waste. The sludges that invariably accompany waste soluble salts are an additional impediment to river dumping.

Public Law 92-500 of the United States reads, in part:

"It is the National goal that the discharge of pollutants into the navigable waters be eliminated by 1985."

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Public Law 94-580 encourages resource recovery on a National scale.

This paper addresses pollutants in the form of soluble salts and resource recovery in the form of water and land. *Ex. 456*

River dumping cannot be considered a satisfactory way for industry to be environmentally clean, even for those industry owners who have access to a river. A method available to inland industry is deep-well dumping. This will handle both solutions and sludges, but it entails capital expense for the well, the pollution of an underground resource, and uncertainty as to where the pollutants will reappear. Various methods of disposal that have been considered are listed below:

1. Sale or reuse
2. Ocean dumping
3. Controlled or secure landfill
4. Under ocean floor burial
5. Deep well injection
6. Encapsulation:
 - a. Pozzolanic landforming
 - b. Deep formation grout injection
 - c. Glass encapsulation
 - d. Plastic encapsulation
7. Chemical fixation
8. Electrolytic conversion
9. Dry-land (desert) storage
10. In-door storage

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The method in this paper is a highly-refined, expertly-arranged instance of pozzolanic landfill with essential previous preparation of the waste. Such preparation is part of the present paper. The method is comprised of a sequence of commercially-available processes to produce a material that is valuable for landform alteration. The sequence was conceived during chemical process planning for a coal conversion process. It applies to numerous other industries and applies world-wide, wherever a minimum amount of water is present to aid in consolidation of the landform.

GASIFICATION OF COAL

The coal process, to convert coal to methane for use as pipeline gas, of the Lurgi type will be used as a basis to explain the disposal process. The purpose of the coal gasification plant is to

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produce methane starting with coal, gasifying it and hydrogenating it. As supplies of low-sulfur coal diminish, coal gasification must operate on high-sulfur coal, and this gives rise to an important section of the complete process. To maintain the integrity of the environment and at the same time to be more efficient, energy-wise, is the challenge of coal gasification. In the Lurgi process, one example out of the many coal gasification processes, lump coal is introduced into the top of the gasifier (3). Steam and oxygen are injected. The resulting high temperature produces a gas which then undergoes a quench-cooling, water-gas shift, hydrogen sulfide and ammonia removal, methanation, compression and dehydration.

The slag or ash is cooled by quench water (including cooling tower and other blowdown water). The condensates from gas cooling and scrubbing lead to coal oils and naphthas as well as phenols, ammonia and aqueous wastes. The removal of acid gases (i.e., carbon dioxide and hydrogen sulfide) result in vented carbon dioxide and a sulfur product such as elemental sulfur, sodium sulfate, or sulfuric acid products that can be kept out of the environment.

WATER USAGE

In this process the basic reaction for producing methane is the reaction of water (steam) with carbon (coal): $2C + 2H_2O = CO_2 + CH_4$. Water from the environment must be supplied for this and for boiler feed water. Rainfall naturally enters the plant site and must be accounted for before it leaves the site. During transit through the coal conversion process, the water is used and re-used several times, but finally it becomes a wastewater and must be treated for disposal to the environment. The proposed disposal process starts with the formation of a "combined feed" to the disposal process proper. To form the combined feed, site runoff (which may include leachate from coal and slag piles) is mixed with the waste water from gas purification. This mixture is wet-oxidized, then polished by filtration through activated carbon. The low-organic effluent which results is made up with softened raw water to become the cooling tower make-up water. The cooling tower blowdown now becomes the waste. The "combined feed" to waste disposal is now formed by adding sulfur recovery waste water, sanitary effluent, boiler blowdowns and ion exchanger blowdowns. A combined feed analysis calculated during the design study showed it would be approximately 1.3 percent total solids, a mixture mainly of sodium sulfate and chloride.

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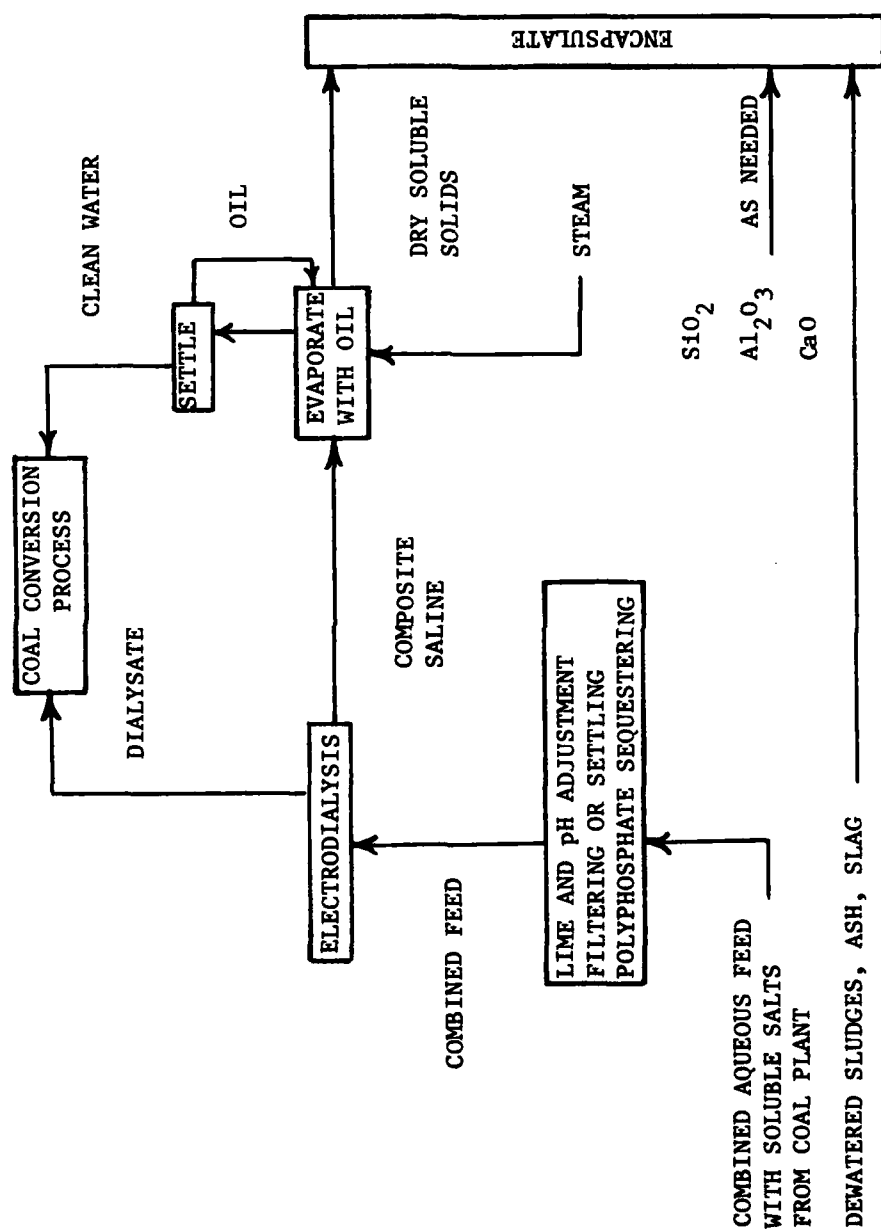
A full-size coal gasification plant is expected to produce 250 million standard cubic feet of methane per day. For this size plant, the combined feed to disposal is approximately 1 million gallons per day (1 MGD), depending upon geographic location and other factors. Larger quantities of water are recycled and are lost by evaporation at the cooling towers. This figure would apply separately to each of the many full-size coal gasification plants required to provide energy self-sufficiency in the United States, this being the objective of the federally-sponsored Project Independence.

DISPOSAL-RECOVERY PROCESS

The proposed disposal-recovery process is shown in Figure 1. Use is made of electrodialysis to recover a large amount of water for reuse in the coal process and to prepare a strong brine. With a strong enough brine it appeared feasible to evaporate economically to a stronger brine or even to dryness in the next step, again recovering water for reuse. The final wet or dry soluble salts are then to be encapsulated by one of several techniques for use in forming a landfill suitable for agriculture, construction, or for any other land use. Pozzolanitic encapsulation is preferred. The sequence of waste treatments proposed here has not been reduced to practice as a totality on a pilot plant or larger scale, although each separate step (such as wet oxidation, electrodialysis, evaporation and encapsulation) has been proved separately in commercial applications. A paper study was therefore made to explore the water treatment outlined above. The general results of the paper design study are presented in this paper.

ELECTRODIALYSIS

Electrodialysis takes salts, the minor constituent, out of water, rather than water from the salts. The electrical energy required is primarily that required only by the salts, the minor constituent, and does not depend primarily on the total bulk of water. A brine results whose strength is theoretically limited only by the solubility of each salt. The method has a high energy efficiency and its proponents have been overcoming the economic limitation of high equipment (membrane and cell) cost. Electrodialysis generates only a minimum amount of wastes and these can be handled downstream. Membranes must be replaced; pumping costs and salt transfer energy are required.



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Figure 1. ED-EV-EN Recovery Process

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A theoretical minimum work of separation can be calculated from the Gibbs free energy of mixing, resulting in 1 BTU per pound of reusable water for the conditions studied. For other conditions, mathematical optimization shows the energy required versus concentration of feed starts from zero for absolutely salt-free water and increases in proportion to the square root of concentration. These "other conditions" include localized parts of the electrodialysis equipment where strong brine is present and is acting as a "feed" (6) in the strong-brine end of the equipment, before being discharged to evaporation. Consequently, the actual energy required will be more than 1 BTU, but will be less than the 1000 BTU required by ordinary evaporation. It is, therefore, possible to recover most of the water by electrodialysis with the expenditure of upwards of 1 BTU per pound of water recovered and the remainder by evaporation, expending downwards of 1000 BTU per pound of water on the remaining few pounds. Increased exit concentration from electrodialysis requires more stages in the process design, with a moderate increase in cost per unit of water recovered. This effect is illustrated in Figure 2.

EVAPORATION

For evaporation in the presence of solid salts, an oil-fluidized process (1) is desirable. By mixing oil with brine, the brine can be evaporated completely to dryness and pressed or centrifuged without thickening, scaling, fouling, or caking. The mixture passes through the evaporator, leaving the solids suspended in the dry oil as fluid slurry. The oil is then centrifuged off to be used again, and the dry solids are left. Water is recovered for reuse in the coal process; its oil is recycled, and the water-soluble solids can emerge in a dry powder form. This form is suitable for encapsulation to permit final disposition of the salts as insoluble forms that will not contaminate water in the environment. The purpose of the oil is to lower the vaporization temperature of the water, to improve heat transfer in the evaporator, to keep the salts suspended so they do not form scale, and to prevent especially scaling and fouling as the salts become completely dry. Water is recovered from condensates to be reused as a recovered resource. The oil evaporation technique is appropriate for a coal conversion plant, as a suitable oil is at hand in the form of one of the products of coal conversion.

For evaporation, the energy consumed is nearly proportional to the quantity of water recovered and is practically independent of feed concentration for a given quantity of water recovered.

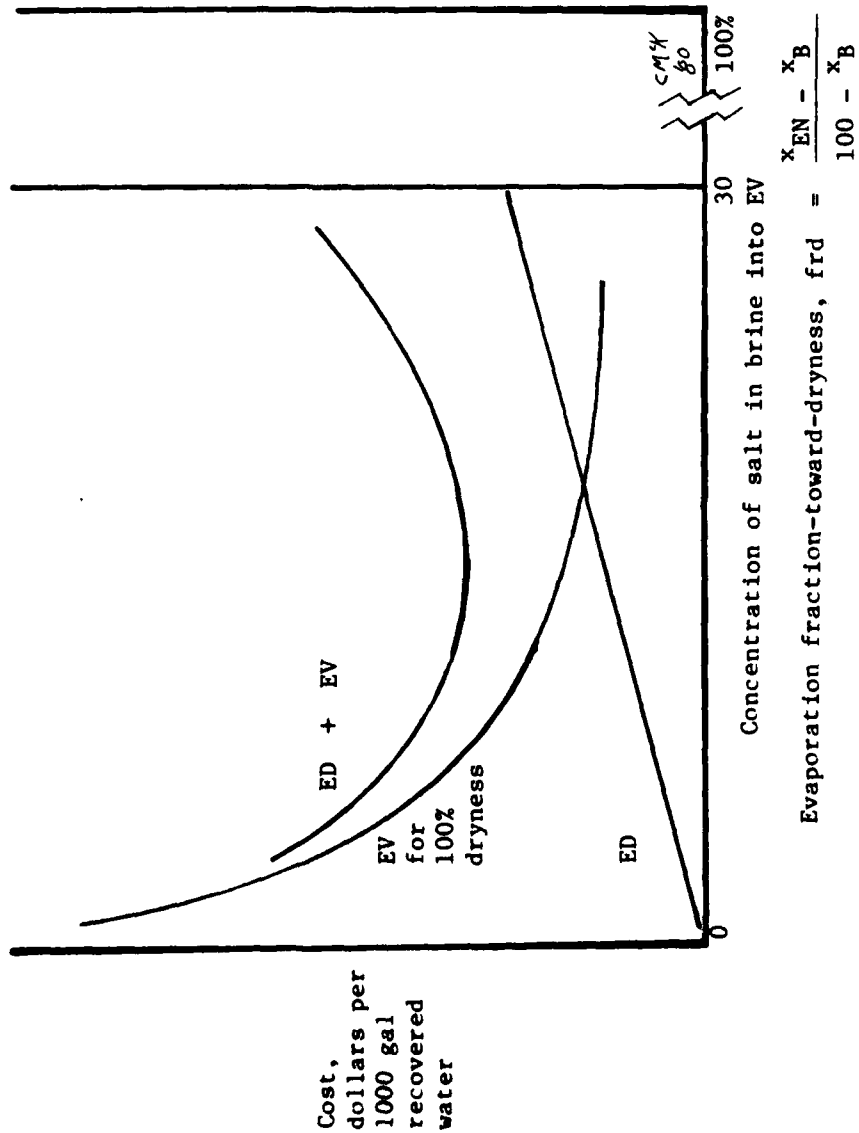


Figure 2. Cost Interactions

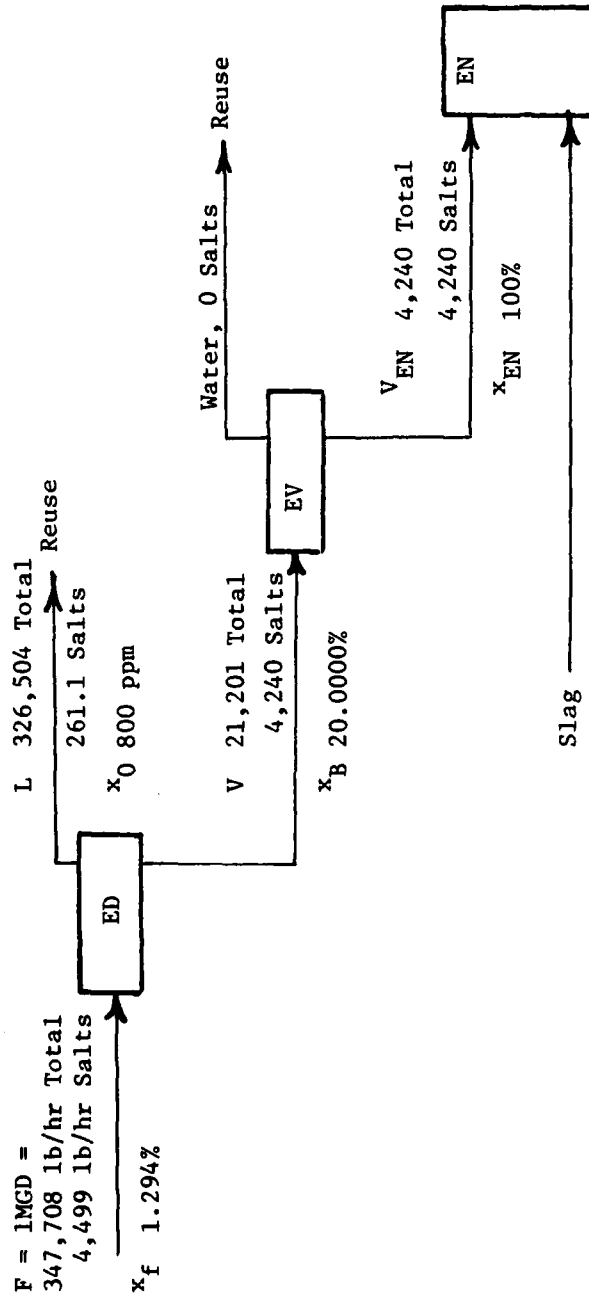
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When evaporator exit concentration is markedly higher than its product water concentration, the boiling point elevation may permit heat economy gain by reusing the heat from one stage in other stages. A mathematical optimization showed that if this effect can be utilized, the optimum number of stages without electrodialysis varies inversely as the square root or less of the concentration level above that of the water condensate (7). Evaporation energy requirements can be explored by merely using an even 1000 BTU per pound for the latent heat of vaporization of water and dividing by the number of effects to incorporate the factor of steam economy. This quick method indicates greater than actual economy for evaporation since boiling point elevation must be added to the temperature drop for heat transfer surfaces to get the actual steam economy. The net result is a slight effect due to concentration. Evaporation remains energy-intensive regardless of concentration. As electrodialysis generates a stronger and stronger brine, the quantity of brine into evaporation lessens. Consequently, the energy and cost of evaporation diminish. The situation is illustrated by the falling evaporation curve on Figure 2, using evaporation to complete dryness for the illustration.

It is noted that Figure 2 shows a rising curve for electrodialysis and a falling curve for evaporation when these operations are operated in series as described above. This situation points to the existence of an optimum cost peculiar to the sequence of these two processes, and it has been verified by design calculations.

Figure 2 was drawn so that the minimum point is at 20 percent, a value selected based on engineering judgment. The exact value must be found by experiment or by a comprehensive design calculation. Regardless of the final correctness of the 20 percent figure, it may be used to illustrate the possible energy savings when electrodialysis preceeds evaporation to dryness (4). A material balance for this case, based on exactly 1 MGD, is shown in Figure 3. The theoretical minimum energy (basis: 1 hour) required is 1 BTU per pound of water times 326,242 pounds of water recovered by electrodialysis plus 1000 BTU per pound of water times 16,961 pounds of water for a total of 17,287,242 BTU per hour. Recovering the same amount of water by evaporation alone requires 1000 BTU per pound times 343,203 pounds of recovered water for a total of 343,203,000 BTU. The comparison is as 19.8:1. If the 1 BTU is increased to 10 BTU to allow for concentration effect, current efficiency, reflux load, pumping and other losses, the comparison is as 16.9:1. As far as a preliminary design study can go, the benefits of using electrodialysis with evaporation seem real.

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Figure 3. Recovery System Material Balance

ENCAPSULATION

The dried soluble salts or strong brine from evaporation are to be encapsulated for permanent storage. Pozzolan encapsulation (2) is a desirable method for accomplishing this. In this method the salts are blended with fly ash, alumina, silica and lime in the proper proportions, and caused to harden as a cement-like monolith of very high density. This can act as a paving landfill, can be used to underlay crop-yielding soil, artificial lakes, building foundations, landscaping forms, etc. The author believes that demilitarization residues can be encapsulated in this manner to prevent leaching if it is required to store them in a moist, non-desert, geographical area. The evaporated salts from the coal process can be considered, as a gross oversimplification, to be equal parts of sodium sulfate and sodium chloride. The sulfate is especially suited to encapsulation by means of the pozzolan method, because one of the most important insoluble compounds formed when the mixture sets up is a calcium sulfo-aluminate. The entire mass is so impermeable that sodium chloride or other soluble salts distributed through it will not be leached out by water and, therefore, will not leach out. A nominal amount of leaching of the external surface occurs and diminishes rapidly with time. There is no leaching from the internal surfaces.

Water can be forced slowly into the fill for experimental purposes if a depth of 90 feet of water is used. This is not likely to happen in the natural environment. Thirty years would be required to fill the small amount of porosity of a 10 foot thick bed under conditions of rainfall of 1/4 inch per 24 hours and 30 inches per year, with no runoff or evaporation. The penetration rate under these conditions is approximately four inches per year of water going in and none coming out. The compacted material as actually used is graded, and drains are installed to permit runoff and to minimize accumulation of standing water. The area required for a commercial-size plant for 20 years (10 feet deep landfill) would be approximately 45 acres. Each section would be settled, compact and stabilized in a matter of months after each last addition. Ashes merely dumped into water can take a long time to stabilize. Unstabilized and "secure" landfills are essentially destroyed land, for some uses.

Compressive strength develops rapidly, so that as a landfill, the completed fill is valuable for nearly every imaginable land use. Because of its strength it can be disposed of at a slope that depends on such considerations as final contour desired and

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retention of cover material rather than on stacking stability. However, before hardening the fill will conform to a wide variety of disposal areas from low flat land along coastal and tidal areas to hilly natural ravines.

Other methods of encapsulation may be indicated in special situations. Sulfur in massive form from the coal plants may have a future use as in divider walls for divided highways. In this case dry soluble salts can be encapsulated in the sulfur. Bituminous road pavings are also capable of encapsulating dry soluble salts.

Encapsulation is considered to be an energy-unintensive operation, but does, nevertheless, have a certain energy consumption. As applied to a coal gasification plant it may encompass slag disposal as well as fly ash and soluble salt disposal. The process starts with slag of suitable particle size and a suitable reactivity, mixes it efficiently with the correct proportion of water and available fly ash and small amounts of additives if necessary. The water may include a certain amount of soluble salts and organics. The mix assumes an earth-like consistency and is then placed in the area to be filled. During several weeks the chemistry of cement formation proceeds, bonding the soluble salts into a stone-like mass, protecting them from extensive weathering. Energy is consumed by transport of slag and water to mixer, slag conditioning, mixing, transport to final emplacement, and consolidation or compaction. The mix should have approximately three parts of slag to one part of liquid (brine). Consequently, the quantity of mix to be handled will depend on the volume of brine from evaporation and not on salt content. All energy and costs in encapsulation will, therefore, depend on the final volume of brine produced. The actual energy required will reflect equipment requirements, in this case conveyors, trucks, and similar earth moving equipment, and most of the energy will go for acceleration and friction in machinery. Grinding slag and solids mixing may also be significant contributors to cost.

THREE-PROCESS SEQUENCE

The three processes exhibit a cost interaction (5). Figure 2 showed an optimum brine concentration feed to evaporation, portrayed for one evaporator condition, viz, 100 percent evaporation of the brine. There is a corresponding optimum for each degree of evaporation. There is a locus of concentrations of effluents from electrodialysis and evaporation under the condition that the salt quantity per unit time is held constant, with the recovered water

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being taken in differing proportions from electrodialysis and evaporation. For any given degree of evaporation and feed concentration, the cost of evaporation will depend on the feed rate to the evaporator. Because of rising electrodialysis cost with rising evaporator feed concentration (Figure 2), and rising evaporation cost with falling concentration, the combined cost, in the general case, shows the same cost at two different values of the feed concentration. The situation is shown schematically in Figure 4, which shows contours of equal cost for various degrees of dryness achieved by evaporation applied to each possible electrodialysis brine effluent concentration. Encapsulation cost is not shown on this schematic because of the possibility of encapsulation using some other source of water and being affected by large quantities of slag, fly ash, other sludges, etc. All contours shift to the left (higher cost) when cost of encapsulation is added. For greater clarity, Figure 4 is a schematic only, and does not show actual costs.

CONCLUSION

In conclusion, a design for disposal of soluble salts has been produced. The interactions of its parameters have been shown by a process design study. The design will enable harmonious compliance with United States Public Laws 92-500 and 94-580, relating to water pollution and resource recovery. In the disposal of waste salt solutions, natural water resources need not be contaminated, because an encapsulation technique is available which will immobilize the salts. At the same time it will make useful landforms available, and water as a resource can be recovered. The bulk of the water can be recovered at a low cost, additional water can be recovered at a higher cost, and the water which must be discarded unavoidably is discarded at a low cost. The waste soluble salts can be provided with an environmentally satisfactory burial.

There is a cost minimum when electrodialysis and evaporation are combined, which is not realizable with evaporation alone, unless very low-cost thermal energy is available or unless very high-cost pretreatment for electrodialysis is required.

All the processes making up the proposed disposal process are commercially available, although they are nowhere operating commercially as one process. Because of the commercial availability of the processes, the proposed process may be a candidate "best commercially available treatment" for soluble salt disposal.

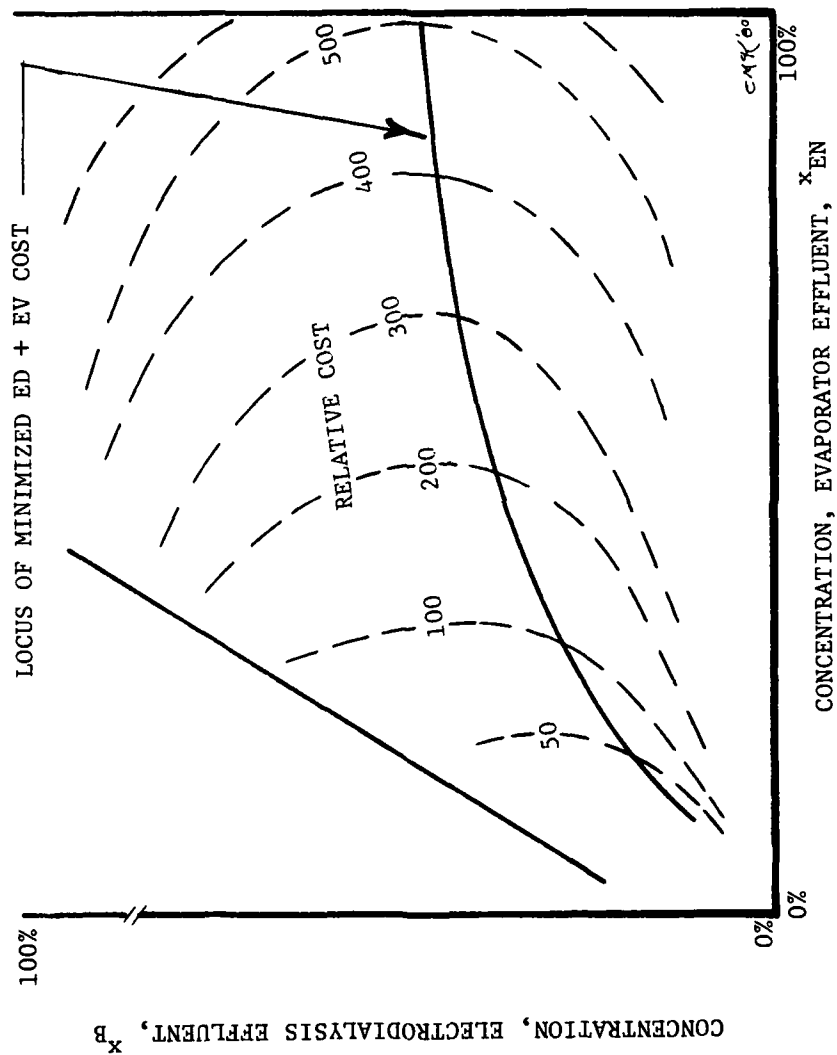


Figure 4. Cost Contours

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